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Inventors: Joseph C. Deaton, Richard L. Parton

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**SYNTHESIS FOR ORGANOMETALLIC CYCLOMETALLATED  
TRANSITION METAL COMPLEXES**

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ATTN: MAIL STOP PATENT APPLICATION  
P.O. Box 1450  
Alexandria, VA. 22313-1450

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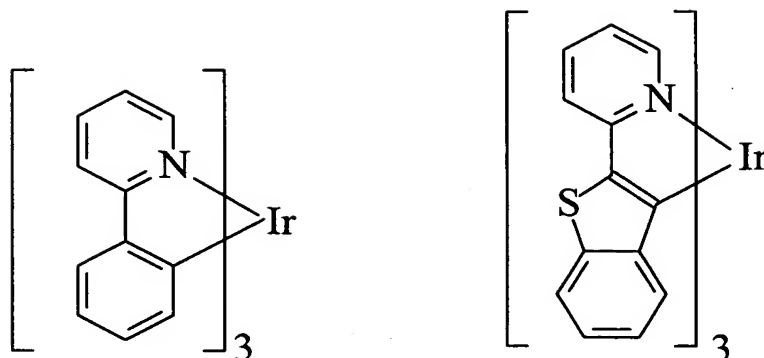
**SYNTHESIS FOR ORGANOMETALLIC CYCLOMETALLATED**  
**TRANSITION METAL COMPLEXES**

**FIELD OF THE INVENTION**

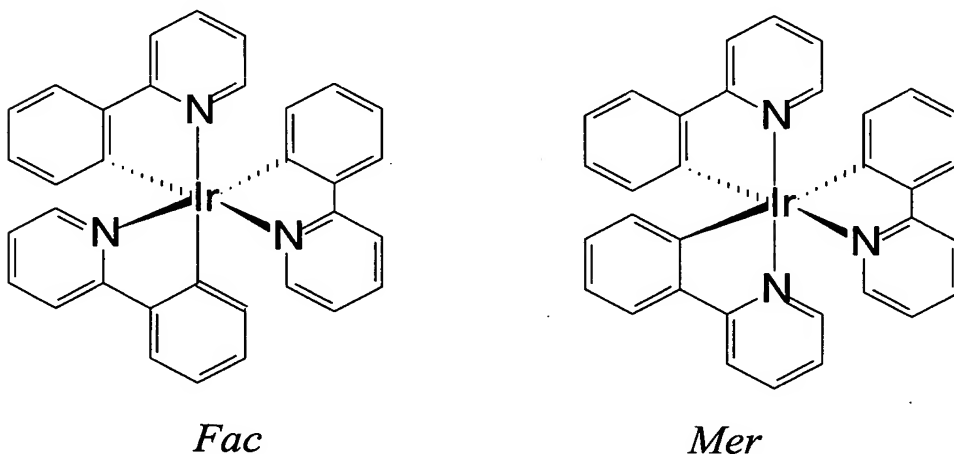
This invention relates to the field of organic synthesis and to a  
5 process for forming organometallic cyclometallated complexes of Ir(III)  
comprising the step of reacting a halide-containing complex of the metal with a  
silver salt and a heterocyclic organic ligand compound capable of forming an  
organometallic cyclometallated complex and in a solvent comprising an organic  
diol.

10 **BACKGROUND OF THE INVENTION**

Organometallic cyclometallated complexes of transition metals  
(e.g. rhodium, iridium, platinum) have become useful materials because of their  
photophysical and photochemical properties. One especially important  
application of these compounds are as phosphorescent dopants in Organic Light-  
15 Emitting Diodes because of their strong emission from triplet excited states (M.A.  
Baldo, et al, *Appl. Phys. Letters*, **75**, 4 (1999)). An important class of  
phosphorescent organometallic cyclometallated complexes contain ligands that  
are at least bidentate wherein one coordination site of the ligand to the metal is  
through an N atom that is doubly bonded to C or another N atom, usually as part  
20 of a heterocyclic ring, and wherein another coordination site of the ligand to the  
metal is through a C atom. As used herein, the term "organometallic  
cyclometallated complex" means that at least one of the coordination sites  
forming the cyclic unit binding the metal atom by at least one ligand must be a  
metal-carbon bond. The metal-carbon bond is formed in place of a hydrogen-  
25 carbon bond of the free ligand before it is complexed. The carbon atom forming  
the metal carbon bond is usually also doubly bonded to another carbon as in, for  
example, a phenyl ring or a thienyl ring or furanyl ring. Further the carbon atom  
forming the metal-carbon bond also is preferably positioned so as to form a five or  
six-membered metallacycle including the coordinated N atom of the ligand. Some  
30 examples of iridium(III) organometallic cyclometallated complexes are shown  
below.



Further, there are two isomers, facial and meridional (*fac* and *mer*); possible for such complexes having three identical but unsymmetrical bidentate ligands as illustrated below. The facial isomers are typically more desirable in OLED applications for having higher quantum yields.



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It is also possible that the organometallic cyclometallating ligands are not all the same. Further, the organometallic cyclometallated complex must have at least one cyclometallating ligand forming a metal-carbon bond, but may have additional types of ligands not forming metal-carbon bonds. A common type of the latter would be complexes of the form  $L_2MX$  as described in WO 02/15645 A1. Here L is a cyclometallating ligand forming metal-carbon and metal-nitrogen bonds, while X is another monoanionic bidentate ligand that does not form metal carbon bonds, such as acetylacetonate.

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The usefulness and importance of organometallic cyclometallated complexes of second- and third-row transition metals have necessitated synthetic methods for preparing them more efficiently. Chassot et al., *Inorg. Chem.*, **1984**, 23, 4249-4253, have used lithiated ligands with platinum compounds that include  
5 leaving groups to form cyclometallated complexes of the ligands with platinum. Joliet et al., *Inorg. Chem.*, **1996**, 35, 4883-4888, also used lithiated ligands to form cyclometallated complexes of the ligands with platinum or palladium, and Lamansky and Thompson, in International Patent Application WO 00/57676, used the same procedure for cyclometallated platinum complexes. These procedures  
10 suffer from low yields, as well as the relative instability of and difficulty in handling lithiated organic materials.

Organometallic cyclometallated complexes may also be formed from direct reaction of the cyclometallating ligand, wherein the carbon-hydrogen is activated and replaced by the carbon-metal bond. For example, *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III), or Ir(ppy)<sub>3</sub>, was made by reaction of 2-phenylpyridine and tris(acetylacetonate) iridium (Ir(acac)<sub>3</sub>) in glycerol solvent by  
15 K. Dedian et al, *Inorg. Chem.*, **30**, 1685 (1991). Sto(e)ssel et al (WO 02/060910 A1) further optimized and improved this reaction, but still using the expensive Ir(acac)<sub>3</sub> starting material. By reacting less expensive halide complexes of Ir(III) such as iridium(III) chloride hydrate with 2-phenylpyridine in a solvent comprising a 3:1 mixture of 2-ethoxy-ethanol and water, Nonoyama obtained dimeric organometallic cyclometallated complexes such as tertakis(2-phenylpyridinato-N,C<sup>2'</sup>-) (di-μ-chloro)di-iridium(III). (Note: Ir(ppy)<sub>3</sub> was later  
20 extracted as a side product in 10% yield from this reaction mixture, K.A. King, et al, *J. Am. Chem. Soc.*, **107**, 1431 (1985).) This particular solvent and the related 2-methoxy-ethanol are not desirable for practical use due to adverse health effects. M.G. Colombo, et al *Inorg Chem.*, **33**, 545 (1994), further reacted the above-cited di-iridium complex with a silver salt in neat 2-phenylpyridine to obtain Ir(ppy)<sub>3</sub> in 75% yield. Grushin et al US 2002/0190250 A1 used this process to make  
30 additional tris-cyclometalated complexes of Ir(III) having fluorine-substitutions on phenylpyridine and phenylquinoline cyclometallating ligands. But this process

requires a large excess of a ligand since it is employed as the solvent, thereby either consuming valuable material or necessitating a process to recover excess ligand.

Lamasky et al., *Inorg. Chem.*, **2001**, *40*, 1704-1711, demonstrated yet another process for making tris-cyclometallated Iridium complexes. First, a mixed ligand complex bis(7,8-benzoquinolinato-N,C<sup>3'</sup>)iridium(III)(acetylacetonate) was made from tetrakis(7,8-benzoquinolinato-N,C<sup>3'</sup>)(di- $\mu$ -chloro)di-iridium(III). Then the bis(7,8-benzoquinolinato-N,C<sup>3'</sup>)iridium(III)(acetylacetonate) was reacted with additional 7,8-benzoquinoline in refluxing glycerol to produce a mixture of isomers of the tris-cyclometallated complex, tris(7,8-benzoquinolinato-N,C<sup>3'</sup>)iridium(III). Kamatani et al, US 2003/0068526 A1, have also employed this reaction type for additional cyclometallated iridium complexes. But this process often yields less-desireable meridional isomers or mixtures of the facial and meridonal isomers of the tris-cyclometallated complexes. Tamayo et al., *J. Am. Chem. Soc.*, **125**, 7377-7387 (2003), have shown that reaction of dimeric organometallic cyclometallated complexes such as tetrakis(2-phenyl-pyridinato-N,C<sup>2'</sup>)(di- $\mu$ -chloro)di-iridium(III) with sodium carbonate and additional cyclometallating ligand in glycerol can lead to formation of meridional isomers in many cases, while further reaction at higher temperatures results in formation of mostly facial isomer. However, this procedure is inconvenient for facial isomers as it necessitates finding exact conditions for the reaction of each ligand.

Despite the large number of investigations into the synthetic methodology for cyclometallated complexes, there remains a need for methods that provide better yields and control of desired isomers.

#### SUMMARY OF THE INVENTION

The invention provides a process for forming an organometallic cyclometallated iridium compound comprising reacting an iridium halide complex with a silver salt and excess organic cyclometallating ligand in a diol solvent.

The process provides better yields and control of desired isomers.

## DETAILED DESCRIPTION OF THE INVENTION

The invention is summarized above. The process reacts an iridium halide complex with the neutral, uncomplexed form of the cyclometallating ligand to form a diiridium cyclometallated complex containing bridging halides and  
5 having formula (1):



wherein L is a bidentate cyclometallating ligand and ( $\mu$ -X) represents a bridging  
10 halide, and then further reacting this intermediate diiridium complex with additional ligand and a silver salt in a solvent comprising a diol. Both steps of the process may optionally be carried out sequentially in the same reaction vessel without first isolating the diiridium intermediate complex. The option of performing both steps in the same reaction vessel provides convenience and  
15 simplification, as long as enough silver salt is added to consume all the halide from the starting material. Alternatively, the diiridium cyclometallated complex formed in the first step comprising the reaction of the cyclometallating ligand with the iridium halide complex may be isolated first, before further reacting in a second step with a soluble silver salt in a solvent comprising a diol. In this  
20 embodiment, the formation of the diiridium cyclometallated complex may be carried out according to the procedure of M. Nonoyama, *Bull. Chem. Soc. Jpn.*, 47, 767 (1974) in which a solvent such as 2-methoxy-ethanol or 2-ethoxy-ethanol in a 3:1 mixture with water is employed. However, there are significant health hazards with the solvents 2-methoxy-ethanol and 2-ethoxy-ethanol, and therefore  
25 it is preferable to use the solvents of this invention for the formation of the diiridium cyclometallated complex as well. Further, it will be appreciated that in the embodiment wherein a diiridium cyclometallated complex is isolated first, and subsequently reacted with additional cyclometallating ligand and a silver salt in a diol solvent, that the additional cyclometallating ligand may be the same or  
30 different from the one already complexed in the starting diiridium cyclometallated complex.

Yet another object of this invention is to provide a process for forming an organometallic cyclometallated iridium compound comprising reacting a complex of the type  $L_2IrX$  with excess organic cyclometallating ligand  $L'$  and in a diol solvent, wherein  $L$  is a cyclometallating ligand forming metal-carbon and metal-nitrogen bonds, while  $X$  is a monoanionic bidentate ligand that does not form metal carbon bonds, and  $L'$  is an organic cyclometallating ligand that may be the same or different from  $L$ . The complexes of the type  $L_2IrX$  may be formed as described in WO 02/15645 A1.

The halide complexes of Ir(III) useful in the invention may be any halide complex or salt thereof, such as for example, iridium(III) chloride hydrate, iridium(III) bromide hydrate, tripotassium hexachloroiridate(III) or tripotassium hexachloroiridate(III). Halide complexes of Ir(IV) may also be used in the invention since these can be readily reduced in the reaction mixture. Examples include dipotassium hexachloroiridate(IV) and dipotassium hexabromoiridate(IV).

The solvents useful in this invention comprise diols. These solvents provide a suitable medium for the organometallic cyclometallation reactions, but are less viscous than for example, glycerol, and therefore it is easier to perform such operations as transfer and filtering. The diol solvents of the present invention also avoid health hazards associated with the 2-methoxy- or 2-ethoxy-ethanol solvents that are frequently used for the cyclometallation reactions. Solvents useful in the invention also provide high product yields and high isomeric purity. The reaction mixtures may be conveniently heated to the reflux temperature of the solvent, or may be held in a constant temperature bath. The preferred temperature range for the reactions is 140 to 220 °C. Examples of solvents useful in the invention include, but are not limited to the following:

Ethylene glycol

1,2-propanediol

1,3-propanediol

1,3-butanediol

catechol

Silver salts useful in the invention include soluble salts with an anion such as tetrafluoroborate, trifluoroacetate, or trifluoromethanesulfonate. It is also possible to use other metal ion salts in the process of the invention if the metal ions form insoluble compounds with halide ions. Examples would be salts of thallium. However, thallium salts are not suitable for manufacturing processes due to the toxic effects of thallium. The reaction vessel may be initially charged with all of the silver salt needed for the reaction, or the silver salt may be added slowly as a solution in additional reaction solvent during the course of the reaction to avoid high concentrations of silver that may lead to reduction of silver.

Furthermore, in one embodiment of this invention where the two reaction steps are conducted sequentially in the same reaction vessel, without isolating the intermediate diiridium complex, the silver salt may all be added in the initial set-up of the reaction vessel, or may be added to the reaction vessel after the first reaction step to form the intermediate diiridium cyclometallated complex is completed.

It is preferable to carry out the process of the invention under an atmosphere of inert gas from which oxygen is excluded to avoid the risk of undesired decomposition reactions with oxygen. The inert gases commonly used for such purposes are nitrogen or argon, but may also be other inert gases such as helium. One simple way to establish the inert atmosphere is to purge the inert gas through the reaction vessels and solvents before starting the reaction. On a small scale, it is also convenient to use a freeze-thaw degas technique in which the initial reaction vessel charged with the starting materials and solvent is frozen while the air is removed by vacuum, followed by introduction of the inert gas atmosphere.

Embodiments of the invention can provide more convenient methods employing less expensive starting materials and solvents that are applicable to a wide range of cyclometallating ligands.

The invention and its advantages can be better appreciated by the following examples.

Example 1. Preparation of *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III)



$K_3IrBr_6$  (7.75 g, 9.82 mmol) was placed in a 200 mL flask with 75 mL 2-ethoxyethanol, 25 mL water, and 2-phenylpyridine (4.2 mL). The mixture was freeze-thaw degassed, and then refluxed for 4 hrs under nitrogen atmosphere during which time a yellow-orange precipitate appeared. After cooling, the precipitate was filtered, washed with 1 N HBr(aq), then water, and dried. Yellow tetrakis(2-phenylpyridine-N,C<sup>2'</sup>)( $\mu$ -dibromo)diiridium(III) (5.018 g) was collected (88% yield based on iridium). This intermediate material was used without further purification in the subsequent step.

Tetrakis(2-phenylpyridine-N,C<sup>2'</sup>)( $\mu$ -dibromo)diiridium(III) (0.960 g) and silver trifluoroacetate (0.54 g) were placed in a 100 mL flask. 1,2-Propanediol (35 mL) and 2-phenylpyridine (0.75 mL) were added and the mixture was freeze-thaw degassed and then refluxed under nitrogen for 5 hours. After cooling, the mixture was poured in air into 150 mL 1molar HBr(aq). The yellow precipitate was filtered, washed with water, and dried. The crude product was sublimed to give yellow-orange powder and crystals (0.982 g) for a 91% yield based on iridium. Analysis by HPLC and combined LC/MS techniques showed the product was *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III) containing only a trace of the meridional isomer.

#### Example 2-7. Additional Preparations of *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III)

Examples 2 thru 7 were carried out in a similar manner to Example 1 except the solvent was changed as listed in Table 1. An additional difference for Examples 3 and 5 was that iridium(III) chloride hydrate was used as the starting material, and hence the intermediate formed in an analogous manner was tetrakis(2-phenylpyridine-N,C<sup>2'</sup>)( $\mu$ -dichloro)diiridium(III). The results shown in Table 1 show that the process with solvents of the invention provide higher yield and better isomeric purity than comparison examples using other solvents, including those commonly found in the prior art of cyclometallation reactions. Example 2 compared to Example 3 further shows that while iridium chloride complexes may be used in the invention as starting materials, better yields may be obtained with the bromide complexes as starting materials.

Table 1.

Example	Example Type	Halide	Solvent	Yield (%)	<i>Mer</i> Isomer(%)
1	Invention	Br	1,2-Propanediol	91	Trace
2	Invention	Br	1,3-Butanediol	89	0.5
3	Invention	Cl	1,3-Butanediol	78	N.A.
4	Invention	Br	Ethyleneglycol	91	1.4
5	Comparison	Cl	2-Ethoxyethanol	56	0.8
6	Comparison	Br	Glycerol	75	14
7	Comparison	Br	1-Octanol	66	Trace

Example 8. Additional Preparation of *fac*-tris(2-phenylpyridinato-

5 N,C<sup>2'</sup>)iridium(III)

This example was also carried out in a similar fashion to example 1, except the solvent was 1,3-propanediol. The yellow precipitate collected was dissolved in dichloromethane and filtered to remove insoluble silver and/or silver salts, and then precipitated by evaporating the solvent. The yield was 92% of tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III), of which the majority was the facial isomer and only 1.2% was identified as the meridional isomer.

Example 9. Synthesis of *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III) In One Vessel.

15 This example was performed in the same manner as example 4 except that both steps in the reaction sequence were carried out sequentially in the same reaction vessel without isolating the intermediate compound and using the 1,3-butanediol solvent from the beginning. 2-Phenylpyridine (1 mL, 1.09 g, 7.0 mmol) and IrCl<sub>3</sub>·3H<sub>2</sub>O (350 mg, 1.0 mmol) were combined with 8 mL of 1,3-butanediol in a 50 mL flask equipped with a magnetic stirrer, condenser and N<sub>2</sub> inlet. The mixture was heated in an oil bath at 170 – 175 °C for 2 hrs with magnetic stirring. A yellow solid formed almost immediately. Silver trifluoroacetate (880 mg, 4.0 mmol) was dissolved in ~2 mL of 1,3-butanediol and

this material was added to the hot reaction mixture using a disposable pipette. A reaction appeared to take place immediately, the yellow solid appeared to dissolve and a new yellow solid appeared to form. The mixture was heated at 170 – 175 °C for an additional 3.5 hr. The heat was removed and after cooling a yellow solid  
5 was collected by filtration, washed with ethanol, and dried (1.07 g). This material was sublimed in a tube furnace with nitrogen entrainment gas (330 °C, 0.7 Torr) to afford 510 mg of product *fac*-tris(2-phenylpyridinato-N,C<sup>2'</sup>)iridium(III) (78% yield). NMR matched the published spectrum.

10 Example 10. Preparation of *fac*-tris-(2-(2'-benzothienyl)pyridinato)Ir(III)

2-(2'-Benzothienyl)pyridine was synthesized according to literature procedures (K.E.Chippendale, B. Iddon, and H. Suschitzky, Journal of the Chemical Society [Section D]: Chemical Communications (1971), 4, 203-4).

K<sub>3</sub>IrBr<sub>6</sub> (5.05 g, 6.40 mmol Ir) and 2.5 equiv 2-(2'-benzothienyl)pyridine  
15 (3.42 g) were placed in a 200 mL r.b. flask with 45 mL of 2-ethoxy-ethanol and 15 mL water. The mixture was freeze-thaw degassed and then refluxed under a nitrogen atmosphere for 6 h. After cooling, a red-orange solid was collected by filtration, washed with 1N HBr(aq) and water, then dried to give 4.23 g of the crude product tetrakis(2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>)(μ-  
20 dibromo)diiridium(III) (95% yield). This material was used without further purification.

A portion of the tetrakis(2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>)di-μ-bromo-  
diiridium(III) complex thus prepared (1.20 g) and 2-(2'-benzothienyl)pyridine  
(0.914 g), and silver trifluoroacetate (0.459 g) were placed under a nitrogen  
25 atmosphere in a 2-neck r.b. flask equipped with a reflux condenser and a rubber septum. 1,3 Butanediol (30 mL) was freeze-thaw degassed in a separate flask and transferred via cannula to the reaction flask. The mixture was refluxed under a  
nitrogen atmosphere for 5 h. After cooling, an orange-red solid was collected by  
filtration in air, washed with 1 N HBr(aq) and water, and dried (1.65 g). This  
30 crude material was triturated with diethyl ether and methanol to remove free  
ligand, affording 1.435 g after drying. This material was dissolved into 30-40 mL  
CH<sub>2</sub>Cl<sub>2</sub> giving a dark red-orange solution with some gray insolubles. The solution

was gravity filtered through a short column of silica gel in methylene chloride. The resulting solution was concentrated until a red-orange solid began to precipitate. Then the rest of the product was driven out of solution by layering heptane and refrigerating. The precipitate was collected by filtration and dried,  
5 0.990 g, 70% yield. The mass spectrum showed parent ion peaks of 822 and 824 amu, corresponding to the two Ir isotopes and confirming the formula tris-(2-(2'-benzothienyl)pyridinato)Ir(III). Part of this material was sublimed at 295-305°C in a tube furnace with nitrogen entrainment gas to yield red-orange crystals. Analysis by HPLC demonstrated that the sublimation had not caused the material  
10 to isomerise. Single crystal x-ray structure determination confirmed that the product was the *fac* isomer.

Example 11. Preparation of *mer*-tris-(2-(2'-benzothienyl)pyridinato)Ir(III)

Tetrakis(2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>)di-μ-bromo-diiridium(III)  
15 (1.64 g,) prepared as in Example 10 was placed in a 100 mL r.b. flask with Na<sub>2</sub>CO<sub>3</sub> (1.25 g). 30 mL 2-ethoxyethanol was added, then 2,4-pentanedione (0.48 g). The mixture was freeze-thaw degassed, then refluxed under N<sub>2</sub> 18 hrs. A dull orange solid was filtered from the dark brown solution, washed with water, and then dried (0.686 g). Analytical data was consistent with the product as bis(2-(2'-  
20 benzothienyl)pyridinato-N,C<sup>3'</sup>)(acetylacetonato)iridium(III) This material was used without purification for the next reaction.

Bis(2-(2'-benzothienyl)pyridinato-N,C<sup>3'</sup>)(acetylacetonato)Iridium(III)  
(0.68 g; 0.954 mmole Ir) as prepared above was placed in a 50 mL r.b. flask with  
25 2-(2'-benzothienyl)pyridine (0.504 g) and about 20 mL 1,3-butanediol. The mixture was freeze-thaw degassed, then refluxed under N<sub>2</sub> 24 hrs. After cooling, a dull red-orange solid was filtered, washed, and dried (0.499g). The mass spectrum showed parent ion s of 822 amu, confirming the formula tris-(2-(2'-benzothienyl)pyridinato)Ir(III). HPLC showed a peak that gave a broad emission at 595 nm but that had a different retention time from that of *fac*-tris-(2-(2'-  
30 benzothienyl)pyridinato)Ir(III) prepared in Example 10. The difference in retention time of the two materials was confirmed by mixing solutions together and observing the two separate peaks in the HPLC and thereby also indicating that

the present crude material consisted of the meridional isomer of tris-(2-(2'-benzothienyl)pyridinato)Ir(III). The crude product was washed with diethyl ether. Then the product was then dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and passed thru a short column of silica gel (15 g) in the same solvent. The red-orange solution was  
5 concentrated and then precipitated by addition of hexanes. An orange powder was collected and dried (280 mg). A portion of this product was sublimed in a tube furnace with N<sub>2</sub> entrainment gas at 288-295°C. Red-orange crystals were recovered. A single-crystal x-ray diffraction study confirmed the structure of *mer*-tris-(2-(2'-benzothienyl)pyridinato)Ir(III), while HPLC analysis showed that the  
10 crystals obtained by sublimation were the same substance as the orange powder before sublimation.

The entire contents of the patents and other publications referred to in this specification are incorporated herein by reference. The invention has been described in detail with particular reference to certain preferred embodiments  
15 thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.